Finding the reconstructions of semiconductor surfaces via a genetic algorithm

F. C. Chuang[1], C. V. Ciobanu[2,3]*, V. B. Shenoy[2], C. Z. Wang[1], and K. M. Ho[1]
[1]Ames Laboratory – U.S. Department of Energy and
Department of Physics, Iowa State University, Ames, Iowa 50011, USA
[2]Division of Engineering, Brown University, Providence, Rhode Island 02912, USA
[3]Division of Engineering, Colorado School of Mines, Golden, Colorado 80401, USA

February 2, 2008

Abstract

In this article we show that the reconstructions of semiconductor surfaces can be determined using a genetic procedure. Coupled with highly optimized interatomic potentials, the present approach represents an efficient tool for finding and sorting good structural candidates for further electronic structure calculations and comparison with scanning tunnelling microscope (STM) images. We illustrate the method for the case of Si(105), and build a database of structures that includes the previously found low-energy models, as well as a number of novel configurations.

*Corresponding author

The determination of atomic structure of crystalline surfaces is a long-standing problem in surface science. Despite major progress brought by experimental techniques such as scanning tunnelling microscopy (STM) and advanced theoretical methods for treating the electronic and ionic motion, the commonly used procedures for finding the atomic structure of surfaces still rely to a large extent on one's intuition in interpreting STM images. While these procedures have proven successful for determining the atomic configuration of many low-index surfaces [e.g., Si(001) and Si(111)], in the case of high-index surfaces their usefulness is limited because the number of good structural models for high-index surfaces is rather large, and may not be exhausted heuristically. An illustrative example is Si(5 5 12), whose structure has been the subject of intense dispute [1, 2, 3, 4] since the publication of the first atomic model proposed for this surface [5]. While the structure of Si(5 5 12) may still be an open problem, there are other stable surfaces of silicon such as (113) [6] and (105) that required a long time for their structures to be revealed; in the present work we focus on Si(105), and show that there is a large number of low-energy models for this surface.

The high-index surfaces attract a great deal of scientific and technological interest since they can serve as natural and inexpensive templates for the fabrication of low-dimensional nanoscale structures. Knowledge about the template surface can lead to new ways of engineering the morphological and physical properties of these nanostructures. The main technique for investigating atomic-scale features of surfaces is STM, although, as pointed out in a recent review, STM alone is only able to provide "a range of speculative structural models which are increasingly regarded as solved surface structures" [7]. With few exceptions that concern low-index metallic surfaces [8, 9], the role of theoretical methods for structural optimization of surfaces has been largely reduced to the relaxation of these speculative models. However, the publication of numerous studies that report different structures for a given high-index silicon surface (see, e.g., [1, 2, 3, 4, 5]) indicates a need to develop methodologies capable of actually searching for the atomic structure in a way that does not predominantly rely on the heuristic reasoning associated with interpreting STM data. Recently, it was shown that parallel-tempering Monte Carlo (PTMC) simulations combined with an exponential cooling schedule can successfully address the problem of finding the reconstructions of high-index silicon surfaces [10]. The PTMC simulations, however, have a broader scope, as they are used to perform a thorough thermodynamic sampling of the surface systems under study. Given their scope, such calculations [10] are very demanding, usually requiring several tens of processors that run canonical simulations at different temperatures and exchange configurations in order to drive the low-temperature replicas into the ground state. If we focus only on finding the reconstructions at zero Kelvin (which can be representative for crystal surfaces in the low-temperature regimes achieved in laboratory conditions), it is then justified to explore alternative methods for finding the structure of high-index surfaces.

In this letter, we address the problem of surface structure determination at zero Kelvin, and report a genetically-based strategy for finding the reconstructions of elemental semiconductor surfaces. Our choice for developing this genetic algorithm (GA) was motivated by its

successful application for the structural optimization of atomic clusters [11, 12]. Like the previous study [10], the present algorithm also circumvents the intuitive process when proposing candidate models for a given high-index surface. Except for the periodic vectors of the surface unit cell [which can be determined from scanning tunnelling microscopy (STM) or from low-energy electron diffraction (LEED) measurements], no other experimental input is necessary. An advantage of the present approach over most of the previous methodologies used for structural optimization is that the number of atoms involved in the reconstruction, as well as their most favorable bonding topology, can be found within the same genetic search. Since the interactions are modelled by empirical potentials, it is generally desirable to check the relative stability of different model structures using higher-level calculations based on density functional theory. Here we test the genetic procedure on the (105) surface, which, at least in conditions of compressive strain, is known to have a single-height rebonded step structure SR [13, 14, 15, 16, 17]. The PTMC study [10] indicates that the SR structure is the lowest surface energy even in the absence of strain, although there are several other reconstructions with very similar surface energies. It is interesting to note that the number of reported reconstructions for the (105) orientation has increased very rapidly from two (models SU and SR [13, 14, 15]), to a total of fourteen reported in Refs. [10, 16]. While the set of known reconstructions has expanded, the most favorable structure has remained the SR model –in contrast with the first reported model [18], but in agreement with more recent studies [13, 14, 15].

Before describing the algorithm, we pause to briefly discuss the computational details. The simulation cell has a single-face slab geometry with periodic boundary conditions applied in the plane of the surface, and no periodicity in the direction normal to it. The top atoms corresponding to a depth $d = 5$Å (measured from the position of the highest atom) are shuffled via a set of genetic operations described below. In order to properly account for the surface stress, the atoms in a thicker zone of 15–20Å are allowed to relax to a local minimum of the potential energy after each genetic operation. In the present work, we test the algorithm for the case of Si(105); the surface slab is made of four bulk unit cells of dimensions[1] $a\sqrt{6.5} \times a \times a\sqrt{6.5}$ ($a = 5.431$Å is the bulk lattice constant of Si), stacked two by two along the [010] and [105] directions. In terms of atomic interactions, we have used the highly-optimized empirical model developed by Lenosky *et al.* [19], which was found to have superior transferability to the diverse bonding environments present on high-index silicon surfaces [10].

The optimization procedure developed here is based on the idea of evolutionary approach in which the members of a generation (pool of models for the surface) mate with the goal of producing the best specimens, i.e. lowest energy reconstructions. "Generation zero" is a pool of p different structures obtained by randomizing the positions of the topmost atoms (thickness d), and by subsequently relaxing the simulation slabs through a conjugate-gradient procedure. The evolution from a generation to the next one takes place by mating, which is achieved by

[1]The lengths of the periodic vectors that correspond to the bulk unit cell are determined from analytic geometry calculations and knowledge of the crystal structure.

subjecting two randomly picked structures from the pool to a certain operation $\mathcal{O}$:(A,B)$\longrightarrow$C. Before defining this operation, we describe how the survival of the fittest is implemented. In each generation, a number of m mating operations are performed. The resulting m children are relaxed and considered for the possible inclusion in the pool based on their surface energy. If there exists at least one candidate in the pool that has a higher surface energy than that of the child considered, then the child structure is included in the pool. Upon inclusion of the child, the structure with the highest surface energy is discarded in order to preserve the total population p. As described, the algorithm favors the crowding of the ecology with identical metastable configurations, which slows down the evolution towards the global minimum. To avoid the duplication of members, we retain a new structure only if its surface energy differs by more than δ when compared to the surface energy of any of the current members p of the pool. We also consider a criterion based on atomic displacements to account for the (theoretically possible) situation in which two structures have equal energy but different topologies: two models are considered structurally different if the relative displacement of at least one pair of corresponding atoms is greater than ϵ. Relevant values for the parameters of the algorithm are $10 \leq p \leq 40$, $m = 10$, $d = 5$Å , $\delta = 10^{-5}$meV/Å^2, and $\epsilon = 0.2$Å.

We now describe the mating operation, which produces a child structure from two parent configurations as follows (refer to Fig. 1). The topmost parts of the parent models A and B (thickness d) are separated from the underlying bulk and sectioned by an arbitrary plane perpendicular to the surface. The (upper part of the) child structure C is created by combining the part of A that lies to the left of the cutting plane and the part of slab B lying to the right of that plane: the assembly is placed on a thicker slab, and the resulting structure C is relaxed. We have found that the algorithm is more efficient when the cutting plane is not constrained to pass through the center of the surface unit cell, and also when that plane is not too close to the cell boundaries. Therefore, we pick the cutting plane such that it passes through a random point situated within a rectangle centered inside the unit cell; numerical experimentation has shown that the algorithm performs very well if the area of that rectangle is about 80% of the area of the surface cell. We have developed two versions of the algorithm. In the first version, the number of atoms n is kept the same for every member of the pool by automatically rejecting child structures that have different numbers of atoms from their parents (mutants). In the second version of the algorithm, this restriction is not enforced, i.e. mutants are allowed to be part of the pool. As we shall see, the procedure is able to select the correct number of atoms for the ground state reconstruction without any increase over the computational effort required for one single constant-n run.

The results for a Si(105) slab with 206 atoms (constant n) are summarized in Fig. 2(a), which shows the surface energy of the most stable member of a pool of $p = 30$ candidates as a function of the number of genetic operations. The lowest surface energy starts at a very high value because the members of early generations have random surface topologies. We find that in less than 200 mating operations the most favorable structure in the pool is already reconstructed, i.e. each atom at the surface has at most one dangling (unsatisfied) bond.

Furthermore, the density of dangling bonds (db) per unit area is the smallest possible for the Si(105) surface: the structure obtained is a double-step model termed DT [10] that has 4 db/$a^2\sqrt{6.5}$. The single-height rebonded structure SR [13, 14, 15] is retrieved in less than 400 mating operations. The SR model is in fact the global minimum for Si(105), as found recently in an exhaustive PTMC search [10]. We have verified this finding by performing constant-n GA runs for a set of consecutive numbers of atoms, $n = 206, 205, 204,$ and 203.

However, we take a further step in that we seamlessly integrate the search for the correct number of atoms within the search for the lowest-energy reconstruction: we achieve this by allowing energetically fit mutants to survive during the evolution, instead of restricting the number of atoms to be constant across the pool. The results from a GA run with variable n are shown in Fig. 2(b), in comparison with an $n = 206$ run. We notice that the variable-n evolution displays a faster drop in the lowest surface energy, as well as in the average energy across the pool. For performance testing purposes, we started the variable-n run with all the candidates having an unfavorable number of particles, $n = 204$: nevertheless, the most stable member in the pool predominantly selected a number of atoms that allows for the SR topology, i.e. n =198, 202, 206 (refer to Fig. 2(c)). While we find no significant difference in the computational effort required by the two different evolutions, the variable-n and the constant-n ($n = 206$), the former is to be preferred: since the surface energy of a Si(105) slab is a periodic function of the number of atoms [10] with a period of $\Delta n = 4$, the variable-n run is ultimately four times faster than the sequential constant-n searches. The results from the sequential runs are summarized in Table 1, which shows the surface energies of twenty structures from runs with n =206, 205, 204, and 203.

Motivated by recent experimental work [20] that suggests the presence of a structure with large periodic length in the $[50\overline{1}]$ direction, we have also performed a GA search for configurations with larger surface unit cells ($2a\sqrt{6.5} \times 2a$), with $n = 406$ atoms. A low-energy (105) reconstruction of this size (termed DR2) was reported in our earlier work [16], where we showed that step-edge rebonding lowers the surface energy below that of the DU1 model proposed in Ref.[20]. Upon annealing, the DR2 model can evolve into three structures with lower surface energies, DR2γ, DR2β and DR2α [10]. Using the GA technique described above, we find structures that are even more favorable than DR2α (refer to Fig. 3 and 4). The results displayed in Fig. 3 indicate that the efficiency of the algorithm improves upon increasing the number of candidates in the pool, from $p = 30$ to $p = 40$. In both cases, the evolution retrieves in the same lowest energy structure with $\gamma = 83.33$ meV/Å^2, which is nearly degenerate with DR2α, as the surface energy difference is only $\sim$0.44 meV/Å^2. It is worth noting that, within the current computational resources, the variable-n algorithm performs quite well even when the number of atoms is doubled. As a test, we have run a variable-n calculation with all the structures in the pool having a number of atoms ($n = 406$) which does not correspond to the optimal configuration: this simulation still retrieves the SR model (global minimum), within about 10^4 genetic operations.

In conclusion, we have shown that the reconstruction of semiconductor surfaces can

be determined via a genetic algorithm. This procedure can be used to generate a database of model configurations for any given high-index surface, models that can be subsequently relaxed using electronic structure methods and compared with available experimental data. The process of systematically building a set of models for a given surface drastically reduces the probability of missing the actual physical reconstruction, which imminently appears when heuristic approaches are used (see, e.g., Refs. [5, 18]). The genetic algorithm presented here can naturally select the number of atoms required for the topology of the most stable reconstruction, as well as the lowest-energy bonding configuration for that number of atoms. Future work will be focused on other high-index silicon and germanium surfaces [4, 21, 22], and on the structure of clusters deposited on silicon surfaces [23].

Acknowledgments. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82; this work was supported by the Director of Energy Research, Office of Basic Energy Sciences. Support from the MRSEC at Brown University (DMR-0079964), NSF (CMS-0093714, CMS-0210095), and the Salomon Research Award from the Graduate School at Brown University is gratefully acknowledged.

References

[1] W. Ranke, Y.R. Xing, Surf. Sci. **381**, 1 (1997).

[2] T. Suzuki, H. Minoda, Y. Tanishiro, K. Yagi, Surf. Sci. **358**, 522 (1996); *ibid.*, Surf. Sci. **348**, 335 (1996).

[3] J. Liu, M. Takeguchi, H. Yasuda, K. Furuya, J. Cryst. Growth **237-239**, 188 (2002).

[4] S. Joeng, H. Jeong, S. Cho, J.M. Seo, Surf. Sci. **557**, 183 (2004).

[5] A.A. Baski, S.C. Erwin, L.J. Whitman, Science **269**, 1556 (1995).

[6] G.D. Lee, E. Yoon, Phys. Rev. B **68**, 113304 (2003).

[7] D.P. Woodruff, Surf. Sci. **500**, 147 (2002).

[8] G. Kresse, W. Bergermayer, R. Podloucky, E. Lundgren, R. Koller, M. Schmid, P. Varga, Appl. Phys. A **76**, 701 (2003).

[9] M. Radecke and E.A. Carter, Phys. Rev. B **51**, 4388 (1995).

[10] C.V. Ciobanu and C. Predescu, Phys. Rev. B **70**, 085321 (2004).

[11] D.M. Deaven and K.M. Ho, Phys. Rev. Lett. **75**, 288 (1995).

[12] K.M. Ho, A.A. Shvartsburg, B.C. Pan, Z.Y. Lu, C.Z. Wang, J. Wacker, J.L. Fye, and M.F. Jarrold, Nature **392**, 582 (1998).

[13] Y. Fujikawa, K. Akiyama, T. Nagao, T. Sakurai, M.G. Lagally, T. Hashimoto, Y. Morikawa, K. Terakura, Phys. Rev. Lett. **88**,176101 (2002).

[14] P. Raiteri, D.B. Migas, L. Miglio, A. Rastelli, H. von Känel, Phys. Rev. Lett. **88**, 256103 (2002).

[15] V.B. Shenoy, C.V. Ciobanu, L.B. Freund, Appl. Phys. Lett. **81**, 364 (2002).

[16] C.V. Ciobanu, V.B. Shenoy, C.Z. Wang, K.M. Ho, Surf. Sci. **544**, L715 (2003).

[17] D.B. Migas, S. Cereda, F. Montalenti, L. Miglio, Surf. Sci. **556**, 121 (2004).

[18] Y.W. Mo, D.E. Savage, B.S. Swartzentruber, M.G. Lagally, Phys. Rev. Lett. **65**, 1020 (1990).

[19] T.J. Lenosky, B. Sadigh, E. Alonso, V.V. Bulatov, T. Diaz de la Rubia, J. Kim, A.F. Voter, and J.D. Kress, Modelling Simul. Mater. Sci. Eng. **8**, 825 (2000).

[20] R.G. Zhao, Z. Gai, W. Li, J. Jiang, Y. Fujikawa, T. Sakurai, W.S. Yang, Surf. Sci. **517**, 98 (2002).

[21] Z. Gai, R.G. Zhao, W. Li, Y. Fujikawa, T. Sakurai, W.S. Yang, Phys. Rev. B **64**, 125201 (2001).

[22] Z. Gai, X. Li, R.G. Zhao, W.S. Yang, Phys. Rev. B **57**, R15060 (1998).

[23] F.C. Chuang, B. Liu, T.L. Chan, C.Z. Wang, K.M. Ho, *Ab initio study of silicon magic clusters on the Si(111)-7×7 surfaces*, to be published.

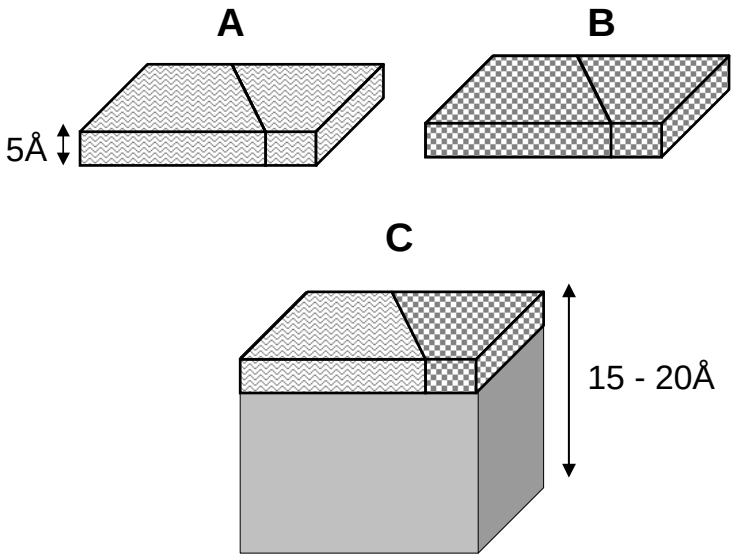

Figure 1: The mating operation $\mathcal{O}$: (A,B) $\rightarrow$ C. From two candidate surface structures A and B, the upper portions (5Å -thick) are separated and sectioned by the same arbitrary plane oriented perpendicular to the surface. A new slab C is created by combining the part of A that lies to the left of the cutting plane and the part of slab B lying to the right of that plane. C is placed on a thicker slab, and the resulting structure is relaxed before considering its inclusion in the pool of candidate reconstructions.

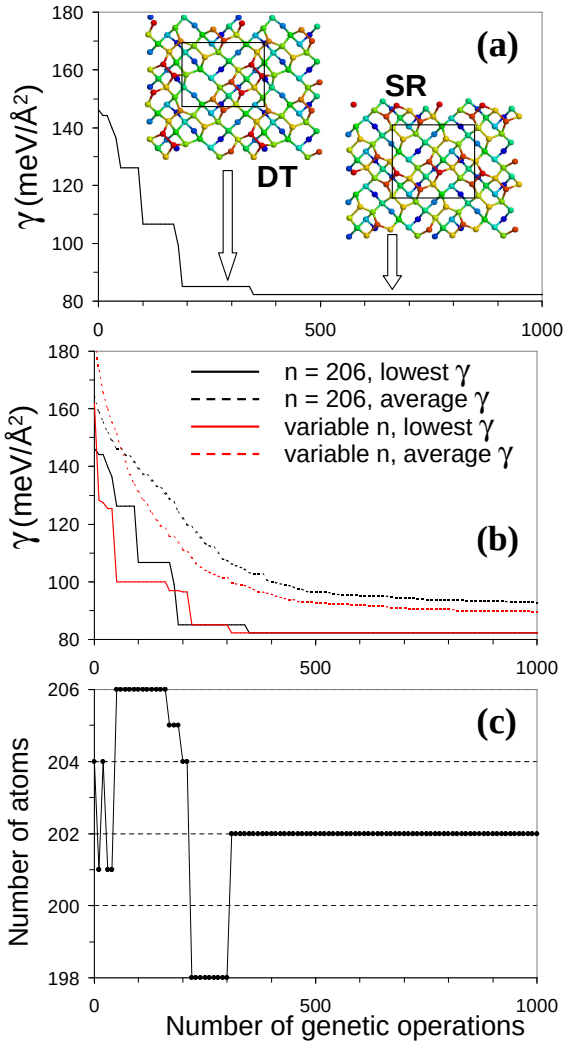

Figure 2: (a) Surface energy γ of the most stable Si(105) candidate from a pool of $p = 30$ structures (206-atom slabs with dimensions $a\sqrt{6.5} \times 2a$), plotted as a function of the number of mating operations. The genetic algorithm quickly retrieves the DT structure [10] and the global minimum structure, SR. The insets show top views (i.e. along the $[\bar{1}0\bar{5}]$ direction) of the DT and SR models; atoms are rainbow-colored according to their coordinate along the [105] direction (red being the highest), and the rectangles show the surface unit cells. (b) Comparison between runs with variable number ($198 \leq n \leq 210$) of atoms (red lines) and constant n, $n = 206$ (black lines). The lowest (average) surface energies are shown as solid (dashed) lines. (c) The variation of the number of atoms of the lowest energy configuration shows that the fittest member of the pool eventually selects a value of n that is compatible with the global minimum structure SR.

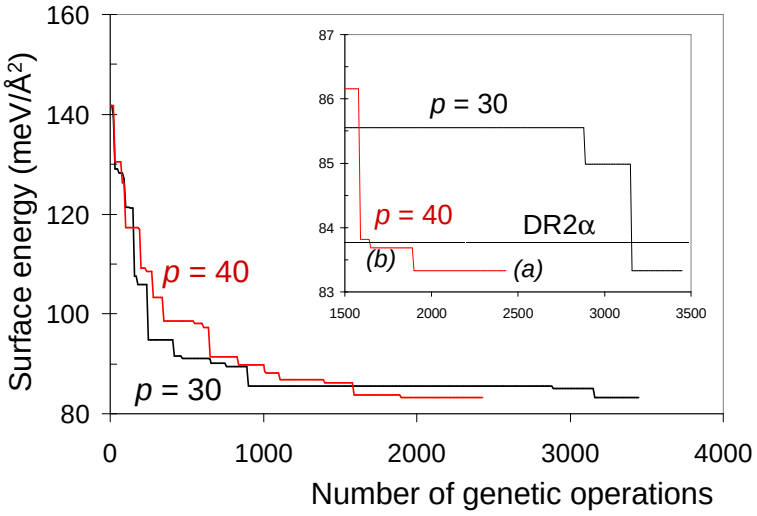

Figure 3: Lowest surface energy γ for pools of $p = 30$ and $p = 40$ Si(105) candidate models. The simulation slab has a periodic cell of $2a\sqrt{6.5}\times 2a$ and contains $n = 406$ atoms, of which the highest-lying 70 atoms are subject to mating operations. As seen in the inset, the procedure finds two structures ((a) and (b)), that are slightly more stable than the DR2α model reported in Ref. [10]; these configurations are shown in Fig. 4, along with DR2α.

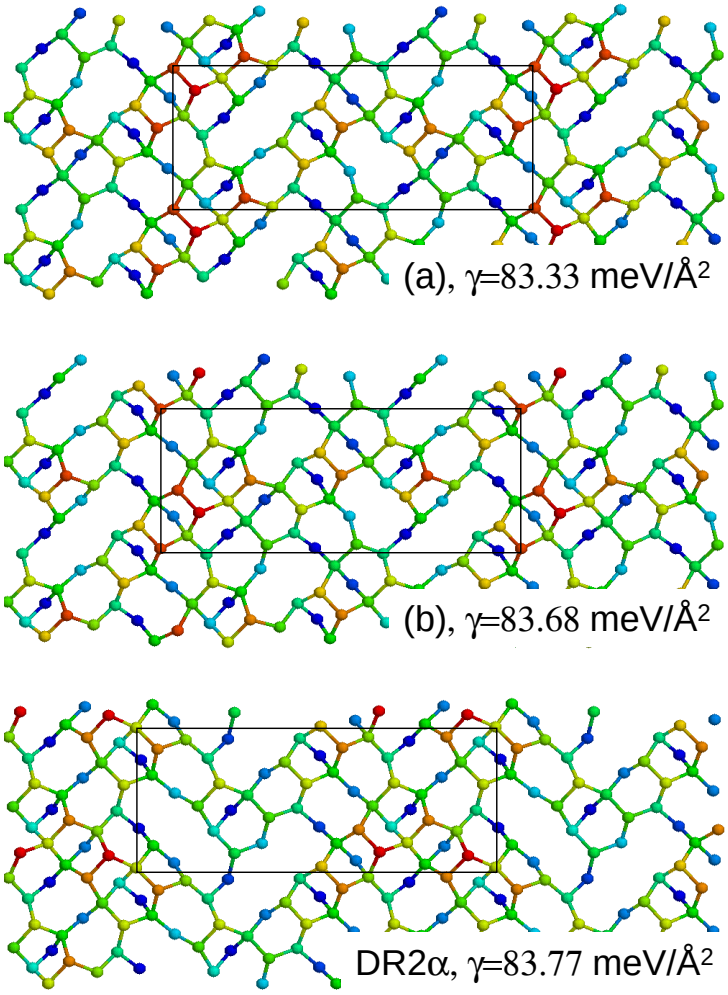

Figure 4: Low-energy structures of the $2a\sqrt{6.5} \times 2a$, 406-atom surface unit cells (rectangles) for Si(105). The surface energies γ are indicated next to the corresponding model labels. Atoms are rainbow-colored according to their height, as described in Fig. 2.

n	Surface energy ($\mathrm{meV/\AA^2}$)	Label from Refs. [10, 16]
206	82.20	SR
	85.12	DT
	88.12	DU1
	88.28	
	88.35	SU
205	86.73	DY1
	88.59	DY2
	88.61	
	88.70	
	88.97	
204	84.90	DX1
	86.04	DX2
	88.98	
	89.11	
	89.78	
203	86.52	DR1
	87.74	
	89.49	
	90.50	
	90.54	

Table 1: Surface energies of 20 different Si(105) reconstructions obtained by the genetic algorithm (GA), calculated using the HOEP interatomic potential [19]. The structures are grouped according to the number of atoms n in the simulation cell. The ground states are the same as those reported in Ref. [10].